18-Crown[6]ether functionalized reduced graphene oxide for membrane-free ion selective sensing

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18-Crown[6]ether functionalized reduced graphene oxide for membrane-free ion selective sensing

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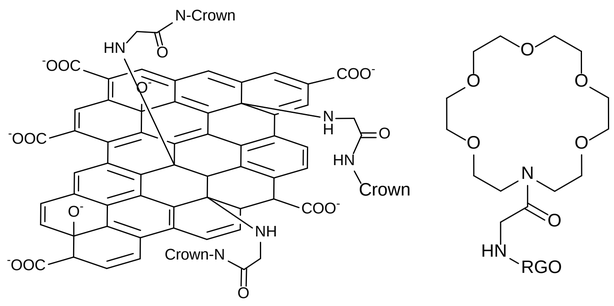
The focus of this work is on the synthesis of a 1-Aza-18-crown[6]ether functionalized reduced graphene oxide (RGO-crown[6]) with specific K^+ binding sites on the RGO surface. Glassy carbon electrodes (GCE) functionalized with RGO-crown[6] weretested for selective potentiometric sensing of K^+, with a detection limit of 10^{-5} M without inference from other ions (Na^+, Li^+, NH_4^+ and Ca^{2+}) in concentrations up to 2.5 × 10^{-2} M. Similar sensing was achieved with functionalized disposable SPE electrodes. The results demonstrate that RGO-crown[6] is a conductive material full of promise for application in fabrication of new types of ion selective sensors.

Introduction

Selective quantitative ion sensors in solution are critical for environmental monitoring and clinical diagnostics. Cost and speed can limit the use of routine quantification in laboratory setting. We attempt to make low-cost disposable sensing devices for use in remote and resource-limited environments. Selectivity towards single ions is essential as most samples contain many different ions. e.g. the K^+ to Na^+ ratio in blood is about 30.

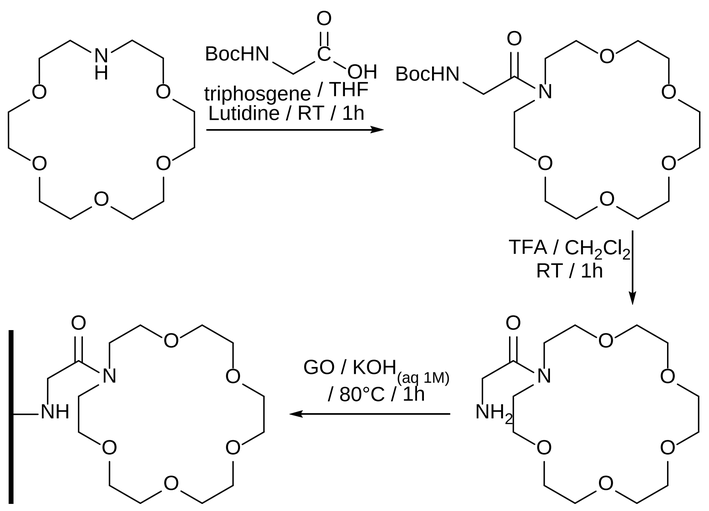
Sensor concept

We utilize potentiometric sensing for our sensor but without a separating membrane by added high concentration of masking salt. The ionophore 18-Crown[6]ether on functionalized RGO ensures selective sensitivity by offering specific binding sites on the electrode.
Reduced graphene oxide is used as support material, because of the easy fabrication and functionalization along with its high specific surface area and conductance making it an ideal material for sensing.

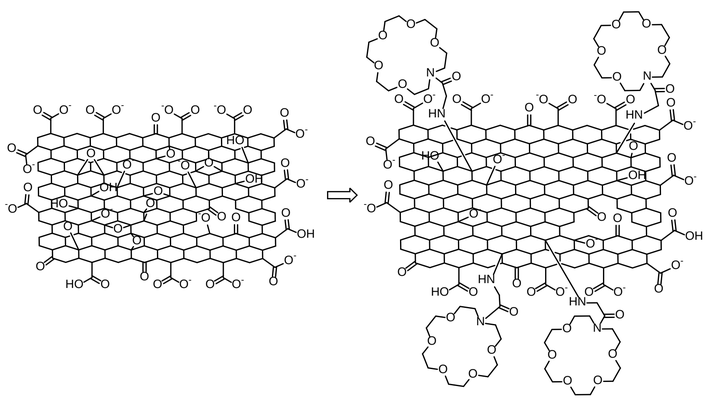


Chemical Synthesis of RGO-Crown[6]

Crown-ether functionalization was prepared by thiophosgene activated peptide coupling of boc-protected glycine linker and 1-aza-18-crown[6]ether followed by deprotection in TFA. GO prepared by modified Hummers' method was then functionalized with this moiety by nucleophilic ring opening of basal plane epoxides under alkaline conditions. Directly following functionalization, GO was reduced in strong alkaline solution at 80 °C. The synthesis procedure is schematically illustrated below.



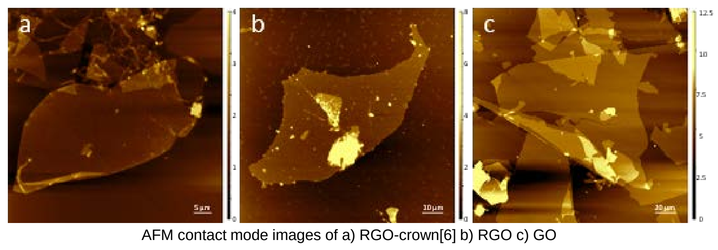
Schematic illustration of synthesis pathway used focusing on molecular change of the crown ether moiety



Schematic illustration of change on the graphene basal plane during synthesis

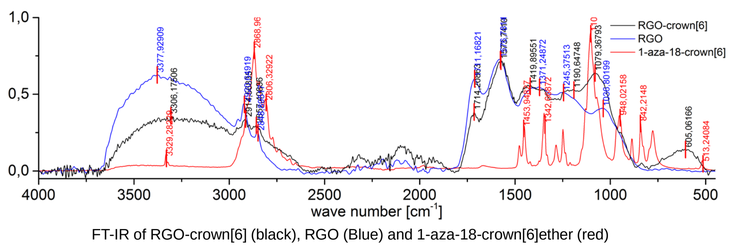
Characterization of RGO-Crown[6]

AFM images of GO, RGO and RGO-crown[6] show that single-layer structural feature is retained during synthesis and RGO nanosheets size does not change significantly.



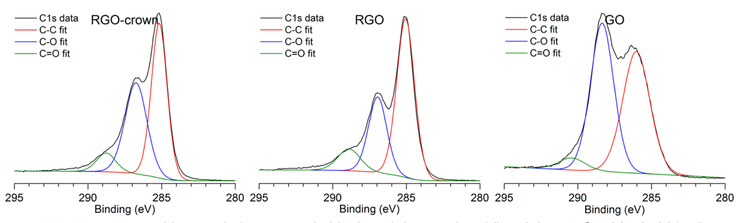
AFM contact mode images of a) RGO-crown[6] b) RGO c) GO

IR spectra of pure 1-aza-18crown[6] reference RGO and RGO-crown[6] indicate that covalent functionalization is achieved.



FT-IR of RGO-crown[6] (black), RGO (Blue) and 1-aza-18-crown[6]ether (red)

The functionalization ratio is determined through XPS from elemental survey 18-crown[6]ether : graphene carbons is 1 : 46. Further evidence of covalent functionalization from C1s spectrum.



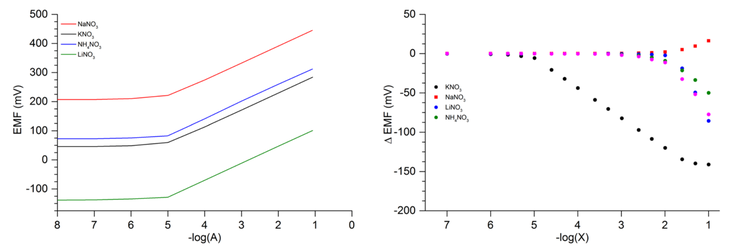
XPS C1s spectra with recorded spectrum in black and deconvoluted fits of data C-C ≈ 284.8 eV (red) C-O ≈ 286 eV (blue) and C=O ≈ 288.5 eV (green) of a) RGO-crown[6], b) RGO and c) GO.

Sample	Survey			C1s			G:O
	%C	%O	%N	C-C	C-O	C=O	
GO	68.8	30.2	1.0	45	47	8	2.2
RGO	75.8	23.8	0.9	60	30	10	3.2
RGO-crown[6]	75.1	21.5	3.4	52	37	11	
Graphene in above	57.8	12.8					4.5

XPS Data table from survey and C1s along with calculated G:O ratio for GO, RGO, RGO-crown[6].

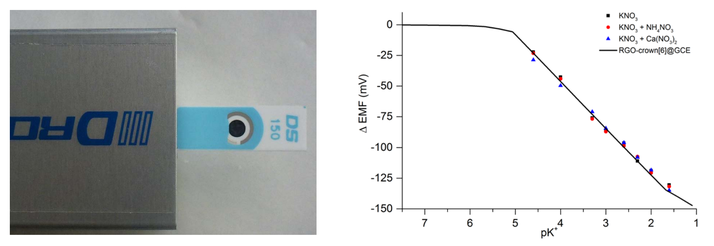
Functional tests of RGO-Crown[6]

The RGO-crown[6] material on GCE was tested for sensitivity and selectivity of Li^+, Na^+, K^+, NH_4^+, Ca^{2+} without masking salt. Nernstian response to potential to all salts but no selectivity was obtained. By adding 100 mM of $NaNO_3$ as masking salt, the response of all ions but K^+ was quenched up to 25 mM. The specific binding of K^+ results in retained sensitivity for K^+ at -37 mV.



Potentiometric titration with nitrate salts for function test of GCE@RGO-crown[6] a) MilliQ b) 100 mM $NaNO_3$

RGO-crown[6] was tested on disposable SPE for sensitivity towards K^+ in pure K^+-solution or with added 10 mM NH_4^+ or 5 mM Ca^{2+}. No effect of NH_4^+ or Ca^{2+} was observed, and respons were largely the same as those on GCE.



a) Picture of disposable SPE with RGO-crown[6] dropcast. b) Response of potential on SPE@RGO-crown[6] from different samples containing K+ either as pure solution or "polluted" with 10 mM NH_4^+ or 5 mM Ca^{2+}.

Summery

- 18-Crown[6]ether modified RGO has been synthesized and characterized sucessfully.
- Sensing of K^+ on GCE has been achieved with a detection limit of 10 µM.
- Selectivity for K^+ has been proven up to the presence of 25 mM Na^+, Li^+, NH_4^+ or Ca^{2+}.
- The material on SPE displayed the same sensing features as that on GCE.

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Acknowledgement

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